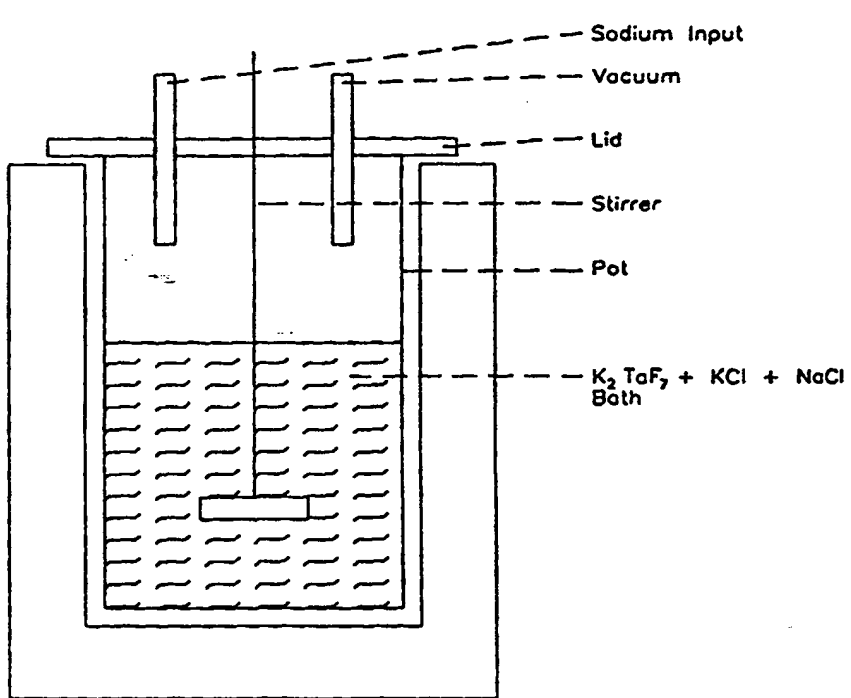


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : C22B 34/24, C23C 14/34</p>	<p>A1</p>	<p>(11) International Publication Number: WO 99/61670</p> <p>(43) International Publication Date: 2 December 1999 (02.12.99)</p>		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(21) International Application Number: PCT/US99/11691</p> <p>(22) International Filing Date: 26 May 1999 (26.05.99)</p> <p>(30) Priority Data: <div style="display: flex; justify-content: space-between; margin-top: 5px;"> 60/086,868 27 May 1998 (27.05.98) US </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> 09/316,777 21 May 1999 (21.05.99) US </div> </p></td> <td style="width: 50%; vertical-align: top; padding: 5px;"> <p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> </td> </tr> </table>			<p>(21) International Application Number: PCT/US99/11691</p> <p>(22) International Filing Date: 26 May 1999 (26.05.99)</p> <p>(30) Priority Data: <div style="display: flex; justify-content: space-between; margin-top: 5px;"> 60/086,868 27 May 1998 (27.05.98) US </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> 09/316,777 21 May 1999 (21.05.99) US </div> </p>	<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(21) International Application Number: PCT/US99/11691</p> <p>(22) International Filing Date: 26 May 1999 (26.05.99)</p> <p>(30) Priority Data: <div style="display: flex; justify-content: space-between; margin-top: 5px;"> 60/086,868 27 May 1998 (27.05.98) US </div> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> 09/316,777 21 May 1999 (21.05.99) US </div> </p>	<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>			
<p>(71) Applicant (for all designated States except US): THE ALTA GROUP, INC. [US/US]; 195 Hartzell Road, Fombell, PA 16123-9518 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): ROSENBERG, Harry [US/US]; 9371 Almar Place, Pittsburgh, PA 15237 (US). OZTURK, Bahri [US/US]; 115 Woodbine Drive, Cranberry Township, PA 16066 (US). WANG, Guangxin [CN/US]; 515 Churchill Court, Cranberry Township, PA 16066 (US). LARUE, Wesley [US/US]; 801 Pinchot Street, Ellwood City, PA 16117 (US).</p> <p>(74) Agent: GIOIA, Vincent, G.; Christie, Parker & Hale, LLP, P.O. Box 7068, Pasadena, CA 91109-7068 (US).</p>				
<p>(54) Title: TANTALUM SPUTTERING TARGET AND METHOD OF MANUFACTURE</p> <div style="text-align: center; margin-top: 20px;">  </div>				
<p>(57) Abstract</p> <p>Described is a method for producing high purity tantalum, the high purity tantalum so produced and sputtering targets of high purity tantalum. The method involves purifying starting materials followed by subsequent refining into high purity tantalum.</p>				

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

TANTALUM SPUTTERING TARGET AND METHOD OF MANUFACTURE

FIELD OF THE INVENTION

This invention relates to a method and apparatus for producing high purity tantalum and the high purity tantalum so produced. In particular, the invention relates to production of high purity tantalum.

BACKGROUND OF THE INVENTION

Tantalum is currently used extensively in the electronics industry which employs tantalum in the manufacture of highly effective electronic capacitors. This is mainly attributed to the strong and stable dielectric properties of the oxide film on the anodized metal. Both wrought thin foils and powders are used to manufacture bulk capacitors. In addition, thin film capacitors for microcircuit applications are formed by anodization of tantalum films, which are normally produced by sputtering. Tantalum is also sputtered in an Ar-N₂ ambient to form an ultra thin TaN layer which is used as a diffusion barrier between a Cu layer and a silicon substrate in new generation chips to ensure that the cross section of the interconnects can make use of the high conductivity properties of Cu. It is reported that the microstructure and stoichiometry of the TaN film are, unlike TiN, relatively insensitive to the deposition conditions. Therefore, TaN is considered a much better diffusion barrier than TiN for chip manufacture using copper as metallization material. For these thin film applications in the microelectronics industry, high purity tantalum sputtering targets are needed.

Most of the tantalum metal produced in the world today is derived from sodium reduction of potassium heptafluotantalate (K₂TaF₇). Processes which are not adapted commercially to any significant extent include the reduction of tantalum oxide (Ta₂O₅) with metallic reductants such as calcium and aluminum, and non metallic reductants carbon and carbon nitrogen; the reduction of the tantalum pentachloride (TaCl₅) with magnesium, sodium or hydrogen; and the thermal dissociation of TaCl₅.

Reduced tantalum is obtained either as powder, sponge or massive metal. It invariably contains significant amounts of oxygen, as well as other impurities such as reductants and impurities that may be present in the starting tantalum compounds. For removal of impurities in tantalum, electron beam melting is often conducted. During electron beam melting, most of the metallic impurities and interstitial gases are vaporized because of their high vapor pressure at the melting point of tantalum (2996°C). Essentially all elements, except niobium, tungsten, molybdenum, uranium and thorium can be eliminated this way. While the metallic impurities and nitrogen are removed by direct volatilization, the removal of oxygen takes place via mechanisms involving formation and evaporation of carbon oxides, aluminum oxides, water, as well as suboxides of tantalum.

1 The purity can be further improved by repeated electron beam melting. Other refining processes include vacuum arc melting, vacuum sintering, molten salt electrorefining and tantalum iodide refining, with the iodide process being the most promising technique for removing tungsten and molybdenum.

5 The above mentioned refining methods are not effective for removal of niobium from tantalum. Since tantalum and niobium are closely associated with each other in nature, the removal of niobium is critical to prepare very high pure tantalum. In practice, their separation is conducted before reduction via methods such as solvent extraction, chlorination and fractional crystallization.

10 The tantalum target manufacturing process includes forging ingot into billet, surface machining billet, cutting billet into pieces, cold rolling the pieces into blanks, annealing blanks, final finishing and bonding to backing plates.

SUMMARY OF THE INVENTION

15 In accordance with the present invention there is provided a method and apparatus for producing high purity tantalum sputtering targets and the high purity tantalum so produced.

The method comprises purifying potassium heptafluorotantalate, K_2TaF_7 , reducing the purified K_2TaF_7 to produce tantalum powder, refining the tantalum by reacting with iodine and finally electron beam melting the tantalum to form a high purity tantalum ingot.

20 The starting material is commercial K_2TaF_7 salt, made by dissolving tantalum ores in hydrofluoric and sulfuric acid mixture, followed by filtration, solvent extraction using methylisobutylketone (MIBK) and crystallization of K_2TaF_7 . This can be repeated several times to lower the impurity levels, in particular the level of Nb.

25 Sodium reduction of purified K_2TaF_7 is conducted in a liquid liquid reduction retort where K_2TaF_7 and diluents (KCl and NaCl) are heated to about 1000°C. Molten sodium is then injected into the retort for reacting with K_2TaF_7 . Agitation of the reactants is provided to accelerate the reduction reaction. After cooling, the mass is taken out of the retort, crushed, leached and washed to separate tantalum powder from the salt mixture.

30 Tantalum refining is done by the iodide process or electron beam melting. These methods can be used in parallel or in series. Electron beam melting is preferred as the last step because it results in an ingot which is suitable for further physical metallurgical steps toward the goal of target manufacture.

35 Electron beam melted ingot is forged into billets and surface machined. After surface machining, the forged billet is cut into pieces, which are further cold rolled into blanks. Blank annealing is carried out in an inert atmosphere to obtain a recrystallized microstructure. The blanks are then machined to obtain a final finish and bonded to copper or aluminum backing plates.

1 For characterization of targets produced by the invented process, chemical analyses are conducted. The methods of chemical analysis used to derive the chemical descriptions set forth herein are the methods known as glow discharge mass spectroscopy (GDMS) for metallic elements and LECO gas analyzer for non metallic elements.

5 The highly purified tantalum material of the present invention has less than 500 ppm by weight, total metallic impurities, an oxygen content of less than about 100 ppm, by weight, a molybdenum or tungsten content of not more than 50 ppm, by weight, and a uranium and thorium content of not more than 10 ppb, by weight. It is also possible to produce tantalum having less than 5 ppm, by weight, total of molybdenum and tungsten.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of the liquid liquid reaction retort used for sodium reduction of K_2TaF_7 ;

Figure 2 is a schematic diagram of an iodide cell;

Figure 3 is a schematic diagram illustration an iodide cell with a distillation unit;

Figure 4A and 4B are schematic diagrams of a tantalum target; and

Figure 5 is a graph of conductance of tantalum bar as a function of time.

DETAILED DESCRIPTION

1) Precursor Purification and Sodium Reduction

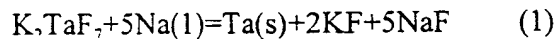
In nature, tantalum generally occurs in close association with niobium, tin and other elements. The minerals most commonly used as raw materials in tantalum production are Tantalite, Wodginite, Microlite and Samarskite. These minerals are enriched by wet gravity, magnetic or electrostatic methods. The concentrates are dissolved in a mixture of hydrofluoric and sulfuric acid. The resulting solution is filtered, then separated from niobium and other impurities in a solvent extraction plant. The tantalum concentrate is transferred into an aqueous solution and precipitated with ammonia to yield tantalum acid ($Ta_2O_5 \cdot xH_2O$), calcined at an elevated temperature to yield tantalum oxide. Alternatively, the tantalum is crystallized to potassium heptafluorotantalate, by addition of KF and KCl to the hot aqueous solution obtained from solvent extraction. Impure potassium heptafluorotantalate obtained by these methods must be further purified for use as a source of tantalum for the electronics industry.

In general, potassium heptafluorotantalate may be purified by a procedure such as follows:

Technical grade potassium heptafluorotantalate (K_2TaF_7) is dissolved in HF, e.g. a 49% HF solution. A mixture of HF and H_2SO_4 can also be used for the

1 dissolution process. The amount of K_2TaF_7 dissolved depends on the temperature and
concentration of HF. Since the dissolution rate is very slow at room temperature, the
mixture is heated e.g. to 90°C in a suitable container. The solution containing K_2TaF_7 is
covered, to prevent losses due to evaporation, and stirred continuously. Time to
5 dissolution is approximately one hour. A 65°C KCl solution is added to the K_2TaF_7
solution and the resulting solution is stirred while cooling to room temperature. The
tantalum in solution precipitates as K_2TaF_7 , since the solubility of K_2TaF_7 is very low at
room temperature. The precipitate is filtered, washed and dried. Niobium, tungsten,
molybdenum, zirconium, uranium and thorium remain in solution. Repeated dissolution
10 and precipitation may be useful in order to obtain extremely high purity tantalum.
Elements such as niobium, tungsten, molybdenum, uranium and thorium, which are
difficult to remove by electron beam melting, are easily removed by this process.

Potassium heptafluorotantalate can be reduced to tantalum metal by fused salt
electrolysis or reduction by sodium. The rate of reduction by electrolysis is very slow,
15 therefore sodium reduction is used for processing large quantities of K_2TaF_7 into tantalum
metal. The overall reduction reaction can be written as



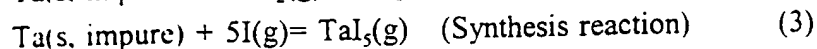
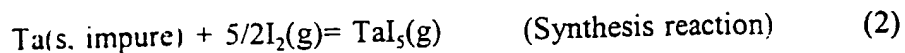
20 Referring to the drawings, FIG. 1 shows a reduction furnace. The reduction is
carried out by placing K_2TaF_7 and some dilute salts such as KCl, NaCl, LiCl, CsCl, $CaCl_2$,
etc. into a reactor equipped with a stirring device. The reactor is placed in a furnace
heated to above the melting point of the salt mixture, usually under 1000°C. Molten
sodium is injected into the reactor and stirred while controlling the temperature. After
25 cooling, the mass is removed from the reactor, crushed and leached with a dilute acid to
recover tantalum metal powder. The powder is compacted and melted in an electron beam
furnace.

2) Iodide Process

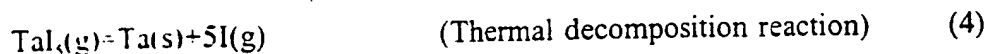
30 Tantalum metal is produced from the reduction of commercially available K_2TaF_7 ,
by sodium, which is a process similar to the Hunter process used for the production of
sponge titanium. The metal produced by the reduction of sodium contains most of the
impurities that exist in the K_2TaF_7 , such as Fe, Ni, Ti, W, Mo, etc. The metal is in the
form of powder and has a very high oxygen content.

35 The method described herein is capable of producing high purity tantalum from
scrap or impure tantalum metal. The process is based on chemical transport reactions, in
which tantalum iodides are formed by the reaction of impure tantalum metal with iodine
gas (synthesis zone), at lower temperatures, then the tantalum iodides are decomposed on a

hot wire filament, at higher temperatures, to produce a very pure metal (deposition or thermal decomposition zone.). The impure tantalum is converted into gaseous species according to the following reactions in the synthesis zone:



Similar reactions can be written for the other tantalum iodide species, such as TaI_3 and TaI_4 . The gaseous species of tantalum diffuse into the thermal decomposition zone and decompose to form pure tantalum metal according to the following reaction:



The thermodynamic factors are important to understanding and controlling the process. Thermodynamic calculations have been carried out to determine advantageous operating conditions, such as temperature and pressure, in the synthesis and decomposition zones.

A schematic diagram of the apparatus is shown in Figure 2. The process apparatus contains a cell, filament and feed material and is designed to run batch operations. After each run the apparatus is cooled to room temperature and disassembled.

The preferred iodide cell, for the refining of tantalum, is an alloy 600 (Inconel) container clad with a metal more electrochemically noble than tantalum according to the chloride electromotive series, such as molybdenum or tungsten or an alloy thereof. The cladding prevents contamination of the refined tantalum by cell components since molybdenum and tungsten do not react with iodine at cell operating temperatures. Alloy 600 (Inconel) containers are also used for the refining of metals such as Ti and Zr, without cladding, since these metals are refined under different operating conditions.

A filament made of pure tantalum rod is used for the decomposition surface. The filament can be in the shape of a U or can be a different shape to increase its surface area. It is also possible to use multiple filaments to increase the surface area and cell productivity. The filament is heated resistively by an external power supply. Since the filament temperature affects the deposition rate, the current is controlled to maintain the filament temperature between 1000 and 1500°C. Tantalum crystals then grow on the filament.

A cylindrical molybdenum screen is placed in the cell to provide an annular space 1 to 3 inches wide. The annular space is filled with tantalum feed material in the form of chips, chunks or small pellets. This type of arrangement gives a high surface area for the reaction between feed material and iodine gas in the cell. The crude tantalum can also be

1 compacted to a donut shape and placed in the reactor. The feed materials are cleaned with
cleaning agents before they are charged into the cell.

A good vacuum system is advantageous to producing tantalum with low impurities.
Therefore, the cell is connected to a vacuum system producing 1 micron or less of
5 pressure. The cell is evacuated at room temperature, then heated to around 800-1000°C
under vacuum to remove all the volatile impurities before iodine is added.

The temperature in the synthesis zone effects the rate of reaction. The temperature
in the synthesis zone should be uniform and kept much higher than boiling point of TaI_5 .
A special heater placed on the lid of the cell keeps the temperature at around 350-500°C,
10 which prevents the condensation of iodides under the lid. Without this heater, iodine must
be continuously added to the system.

Oxygen in tantalum originates from numerous sources, starting with the precursor
and on through electron beam melting. Oxygen is undesirable at high concentrations due
to its effect on the resistivity of deposited tantalum thin films. Currently available
15 methods cannot easily decrease the oxygen levels to less than 30 ppm. Thermodynamic
calculations, as well as the experimental results, indicate that the metal oxides formed or
present in the feed material do not react with iodine and are not transported to the
decomposition zone. Therefore, this process is capable of producing high purity tantalum
with very low oxygen. The amount of oxygen remaining in the cell atmosphere is reduced
20 by a combination of argon flushing and vacuum. Nitrogen in the feed material behaves
like oxygen, therefore the nitrogen content of tantalum crystal bar will be very low.

Electron beam melting is frequently used to refine tantalum. However, electron
beam melting cannot remove elements such as tungsten and molybdenum, since the vapor
pressures of these elements are very low at the melting temperature of tantalum. The
25 present process is capable of consistently removing elements such as tungsten and
molybdenum to extremely low levels. The process may also remove uranium and thorium,
which cannot be removed by electron beam melting.

The iodide process described above may not be able to remove significant amounts
of niobium. Therefore, the current process has been modified to obtain pure tantalum with
30 very low metallic impurities including niobium. In the modified process, tantalum scrap
or crude tantalum is reacted with iodine gas to form gaseous TaI_5 and NbI_5 , which then are
separated by fractional distillation, since the boiling points of these two compounds are
different. A schematic of the apparatus is shown in Figure 3.

Crude tantalum or scrap is placed in a vertical tube made of Inconel and clad with
35 molybdenum, tungsten or an alloy thereof. The tube is placed in a furnace that is heated
to 400-700°C. A carrier gas such as clean argon or helium is passed over an iodine bath.
The temperature of the bath is adjusted to get a specific I_2 partial pressure. Iodine gas
reacts with tantalum scrap to produce gaseous tantalum and niobium iodide. The gas from

1 the feed reactor passes through the distillation columns. The temperature of the first
column is maintained just below the boiling point of TaI_5 , to condense TaI_5 . The second
column is maintained at a temperature low enough to condense NbI_5 , but above the boiling
point of I_2 . The iodine gas is circulated through the process of reuse. All the gas lines
5 between the first column and furnace are made of molybdenum and maintained at about
600°C, the others are maintained at lower temperatures.

The pure liquid or solid TaI_5 obtained from the fractional distillation unit is fed into
the deposition reactor and the TaI_5 decomposes on a hot surface to produce pure tantalum
crystals. Tantalum obtained from this process is very pure and free of all impurities that
10 cannot be removed by conventional processes. The pure tantalum obtained by the
modified iodide process is electron beam melted to produce high purity tantalum ingots.

3. Electron Beam Melting

Electron beam melting is commonly used to melt and refine refractory materials.

15 The process is based on the use of the intense heat generated when a high energy
particle stream impinges on a material, transforming its kinetic energy into thermal energy.
The flexibility to distribute energy yields a large number of electron beam melting
techniques such as button, drip, hearth, zone melting, etc. for various metals. Electron
beam hearth melting has been established for titanium and super alloys. Electron beam
20 drip melting may be used for refractory materials. An electron beam drip melting furnace
comprises a horizontal bar feeder for primary feedstock. The bar feeder is equipped
with a vacuum valve which allows nearly continuous feeding and melting of precompacted
materials. The refining of refractory metals occurs via vaporization of suboxides,
evolution and removal of gases, carbon-oxygen reaction and vaporization of metallic
25 impurities. Most of the elements can be removed from tantalum during melting by the one
of above mechanisms. However, electron beam melting cannot remove W, Mo, Nb, U, Th,
etc. due to low vapor pressures of these elements at the melting temperature. Repeated
melting may be necessary to get very high purity materials.

30 Scrap, impure tantalum, tantalum powder obtained from electrolysis or reduction of
 K_2TaF_7 , is compacted and melted in an electron beam drip melting furnace to produce high
purity tantalum ingots.

4. Target Manufacturing

35 Ingots obtained from electron beam melting are forged into billets and surface
machined. After surface machining, the forged billet is cut into pieces, which are further
cold-rolled into blanks. The blanks are annealed in an inert atmosphere to obtain the
desired microstructure. The blanks are then machined to obtain the final finish and may be
bonded to copper or aluminum backing plates. A schematic of the target produced is

shown in Figures 4A and 4B.

It is desirable to perform a chemical analysis and characterization of targets by measuring the grain size and texture. The methods of chemical analysis useful to derive the chemical descriptions set forth herein are the methods known as glow discharge mass spectroscopy (GDMS) for metallic elements and LECO gas analyzer for non-metallic elements. Line interception method is used for grain size determination and XRD and EBSD are used to obtain texture data.

EXAMPLE 1

About 350 grams of K_2TaF_7 was added to 595 cc of HF (49%) in a Teflon beaker. The mixture was heated to 90°C and stirred continuously. The beaker was covered with a Teflon plate to prevent evaporation of the solution. The dissolution process lasted about one hour. About 140 grams of KCl was dissolved in 700 cc of distilled water and heated to 60 C. The KCl solution was added to the K_2TaF_7 solution and the resulting solution was stirred for several minutes. The solution was cooled to room temperature which caused the tantalum in the solution to be precipitated as K_2TaF_7 , since the solubility of this compound is very low at room temperature. The precipitates were filtered and washed with KF solution (100 gr/liter H_2O) and distilled water. The powder was dried at 160°C in a vacuum furnace, then analyzed for composition. X-ray diffraction studies were carried out on the precipitates.

Several examples were carried out according the procedure described above and samples were analyzed. The niobium content of K_2TaF_7 was reduced by 50 percent after the first treatment. The results are shown in Table 1. The data shown in Table 1 indicates it is possible to decrease the niobium content of tantalum by this method. The purified K_2TaF_7 may be reduced by sodium.

Table 1

Element	Original K_2TaF_7	K_2TaF_7 After First Wash	K_2TaF_7 After Second Wash
Nb	4.6	<2.2	<1
Mo	0.2	0.1	0.1
W	4.8	1.1	<1
Zr	0.52	0.14	<0.1
Th	<0.01	<0.01	<0.01
U	<0.01	<0.01	<0.01
Na	1100	130	50
Fe	4.8	1.2	<1
Al	2.5	1.2	
S	8.7	1.1	

The data in Table 1 has shown that the contents of Nb, Mo and W are largely lowered by this method. It is well known that these elements cannot be removed from Ta metal by electron beam melting. Therefore, a removal of these three elements from the

K_2TaF_7 is beneficial to producing very pure tantalum. Assuming all Nb, Mo and W in the K_2TaF_7 will be co-reduced with Ta in the sodium reduction stage and neglecting the existence of all other elements listed in Table 1, a simple calculation can be made to show the influence of the K_2TaF_7 purification on metal purity. A complete sodium reduction of 1000 g of original K_2TaF_7 would produce 461.7 g of Ta which would contain 9.6 mg of Nb, Mo and W, resulting in a metal purity of 99.9979%. When using 1000 g twice washed K_2TaF_7 , 461.7 g of Ta produced by sodium reduction would contain less than 2.1 mg of Nb, Mo and W. The metal purity would then be 99.9995%.

EXAMPLE 2

An iodide cell was used to produce pure tantalum from scrap available in the market. The cell was made of an Inconel alloy and lined with molybdenum for the preliminary experiments. A molybdenum screen was placed inside the cell and Ta scrap was used to fill the gap between the screen and the cell wall. The cell was leak checked, then evacuated to below 10 microns. The cell was heated to 850 C. under vacuum, to evaporate and remove organic and other volatile compounds. Then the cell was cooled to room temperature and the precipitates on the lid were cleaned. A filament made of pure Ta was installed on the cell lid. The cell was sealed and evacuated to below 10 microns again. The feed was heated to about 500-600°C and the filament to 1000-1200 C. When the feed and filament temperature were stabilized, a measured quantity of iodine crystals were added to the reaction chamber. The current and voltage supplied to the filament were measured continuously. From these values it is possible to calculate the conductance, which is related to the diameter of the bar. The vessel pressure, and filament and feed material temperatures were controlled. Tantalum bars are successfully grown by this method.

It was found that the temperature of the filament and feed as well as the pressure affects the deposition rate significantly. The growth rate of Ta bar is related to conductance of Ta bar. The growth rate in terms of conductance (Mho) is shown in Figure 5. Very high deposition rates are obtained by this method as shown in Figure 5. Chemical analyses of the resulting tantalum bars from several runs are given in Table 2. It must be noted that scrap used in the experiments was not homogenous in composition. The original composition of the tantalum feed material is also shown in Table 2.

Table 2

		Run 1	Run 2		Run 3	Run 4
Time, hrs		79	45		62	45
Weight, gr		5925	5043		7829	5969

Element (ppm)	Feed 1 & 2	Run 1	Run 2	Feed 3 & 4	Run 3	Run 4
Nb	1200	900	505	90	185	230
Mo	6	1.2	1.7		1.3	1.2
W	30,000	0.28	0.19		0.2	0.25
O	100	90	308	100	60	176
N	100	<10	3	100	6	4

EXAMPLE 3

Tantalum crystal bars from various runs were melted in an electron beam furnace. The analytical results of the tantalum feed stock and the melted tantalum ingot are shown in Table 3.

Table 3

Element	Feed Material Concentration (Average ppm)	Concentration After Melting (Average ppm)
Fe	344	1
Ni	223	0.13
Cr	205	0.19
Nb	463	270
O	221	<25

EXAMPLE 4

Ingots obtained from electron beam melting are cold worked and annealed to produce target blanks. Initial ingot breakdown is done via a combination of side and upset forging. After surface machining, the forged ingot is cut into pieces, which are further cold rolled into blanks. Two rolling temperatures are considered: room temperature and liquid nitrogen temperature. The former is called cold rolling, while the latter is referred to as cryogenic rolling. The reduction at rolling is in the range of 70 to 90%. The rolled blanks are annealed in an inert atmosphere or vacuum under different conditions to obtain the desired microstructure and texture.

EXAMPLE 5

Blanks with fine grains and desired texture are machined to obtain the final finish and bonded to copper or aluminum backing plates. A schematic of the target produced is shown in Figures 4A and 4B.

In the foregoing discussions, it is apparent that various changes and modifications may be made within the preview of the invention. Accordingly, the scope of the invention should be limited only by the appended claims.

1 CLAIMS:

1. A method for producing high purity tantalum comprising the steps of:
purifying K_2TaF_7 by a dissolution process;
reacting purified K_2TaF_7 with a reducing agent to produce tantalum powder;

5 and

reacting said tantalum powder with iodine in a container.

2. A method according to claim 1, wherein HF or a mixture of HF and H_2SO_4 is used in the dissolution of K_2TaF_7 .

10 3. A method according to claim 1, wherein a solution containing KCl is used to precipitate said K_2TaF_7 from the solution.

15 4. A method according to claim 1, wherein Nb and other metallic impurities in said K_2TaF_7 are reduced to levels lower than about 20 ppm, by weight.

5. A method according to claim 1, wherein W and Mo in said K_2TaF_7 are reduced to less than about 1 ppm, by weight.

20 6. A method according to claim 1, wherein said reducing agent is sodium.

7. A method according to claim 1, wherein said container has a reactant-contacting surface comprising a metal more electrochemically noble than tantalum according to the chloride electromotive series.

25 8. A method according to claim 7, wherein said reactant-contacting surface comprises molybdenum, tungsten or an alloy of molybdenum and tungsten.

30 9. A method according to claim 1, further comprising electron beam melting said tantalum to produce a high purity tantalum ingot.

10. A method for producing high purity tantalum comprising reacting impure tantalum with iodine gas in a container and decomposing tantalum iodides on a filament.

35 11. A method according to claim 10 wherein said container has a reactant-contacting surface comprising a metal more electrochemically noble than tantalum according to the chloride electromotive series.

- 1 12. A method according to claim 11 wherein said reactant-contacting surface
comprises molybdenum, tungsten or an alloy of molybdenum and tungsten.
13. A method according to claim 10 wherein said filament comprises tantalum.
- 5 14. A method according to claim 10 further comprising electron-beam melting
said tantalum to form a high-purity tantalum ingot.
15. High purity tantalum comprising tantalum and less than about 500 ppm, by
10 weight, total metallic impurities.
16. High purity tantalum comprising less than about 50 ppm, by weight, tungsten
or molybdenum.
- 15 17. High purity tantalum comprising less than about 20 ppm, by weight, tungsten
or molybdenum.
18. High purity tantalum comprising less than about 5 ppm, by weight, each of
tungsten and molybdenum.
- 20 19. High purity tantalum comprising less than 20 ppm, by weight, total of
niobium, molybdenum and tungsten.
20. High purity tantalum comprising tantalum and less than 5 ppm, by weight,
25 total of niobium, molybdenum and tungsten.
21. A sputtering target comprising high purity titanium according to claim 15.
22. A sputtering target comprising high purity titanium according to claim 16.
- 30 23. A sputtering target comprising high purity titanium according to claim 17.
24. A sputtering target comprising high purity titanium according to claim 18.
- 35 25. A sputtering target comprising high purity titanium according to claim 19.
26. A thin film produced by a sputtering target according to claim 15.

- 1 27. A thin film produced by a sputtering target according to claim 16.
28. A thin film produced by a sputtering target according to claim 17.
- 5 29. A thin film produced by a sputtering target according to claim 18.
30. A thin film produced by a sputtering target according to claim 19.

10

15

20

25

30

35

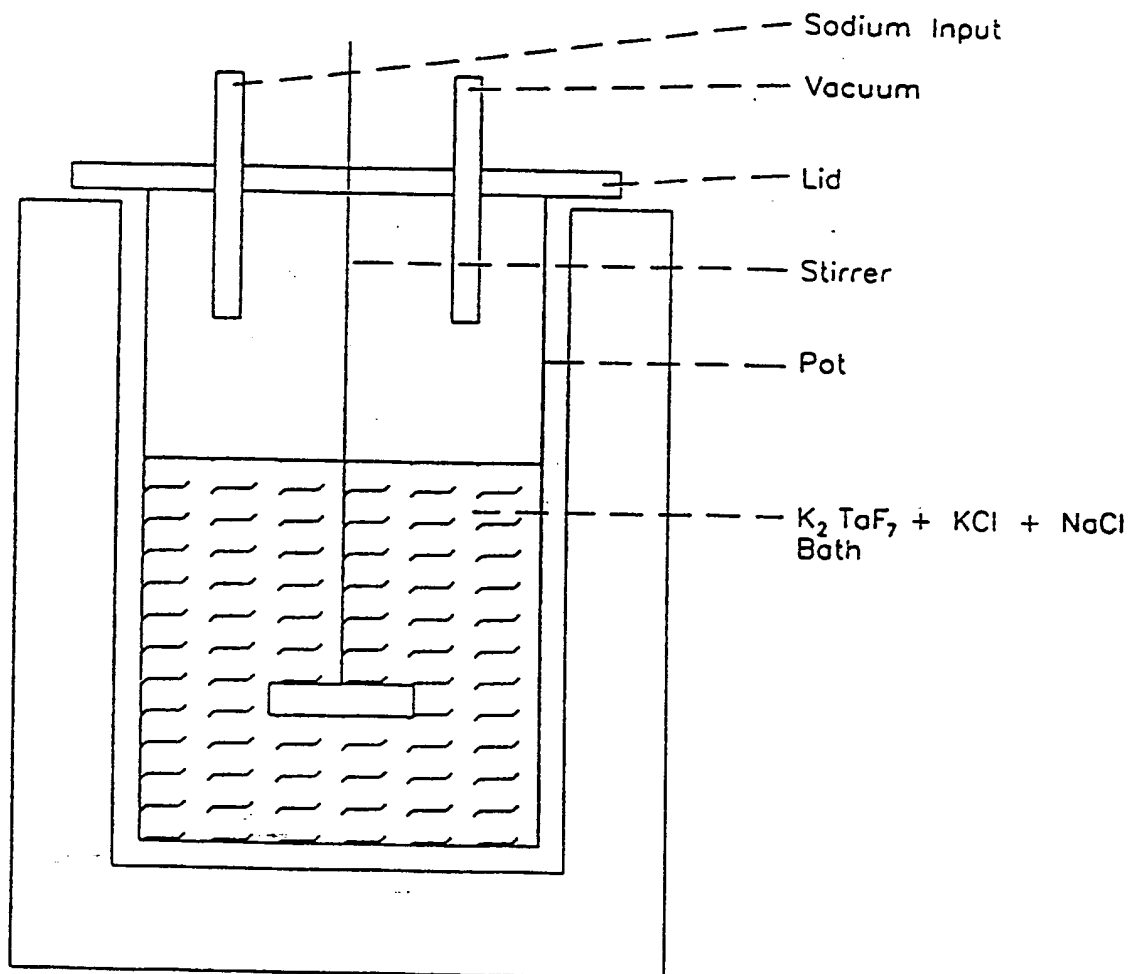


FIG. 1

2/5

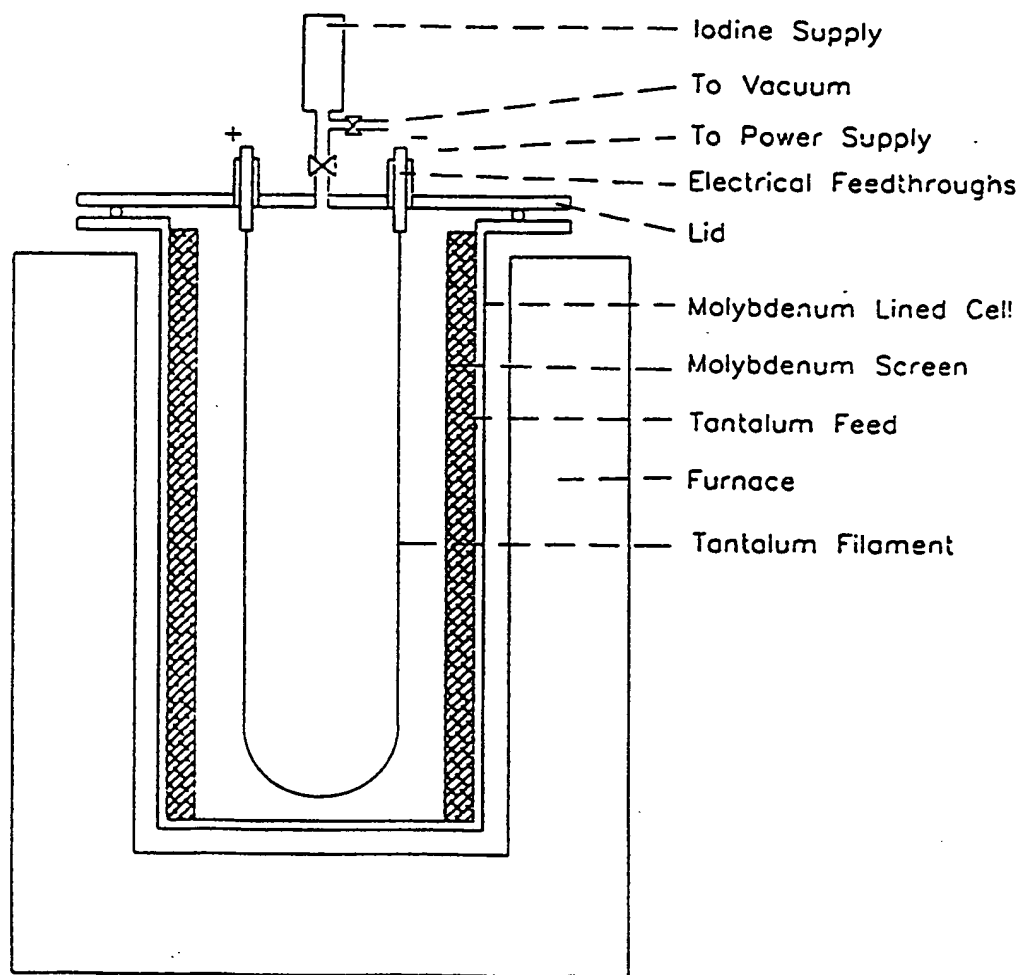


FIG. 2

3/5

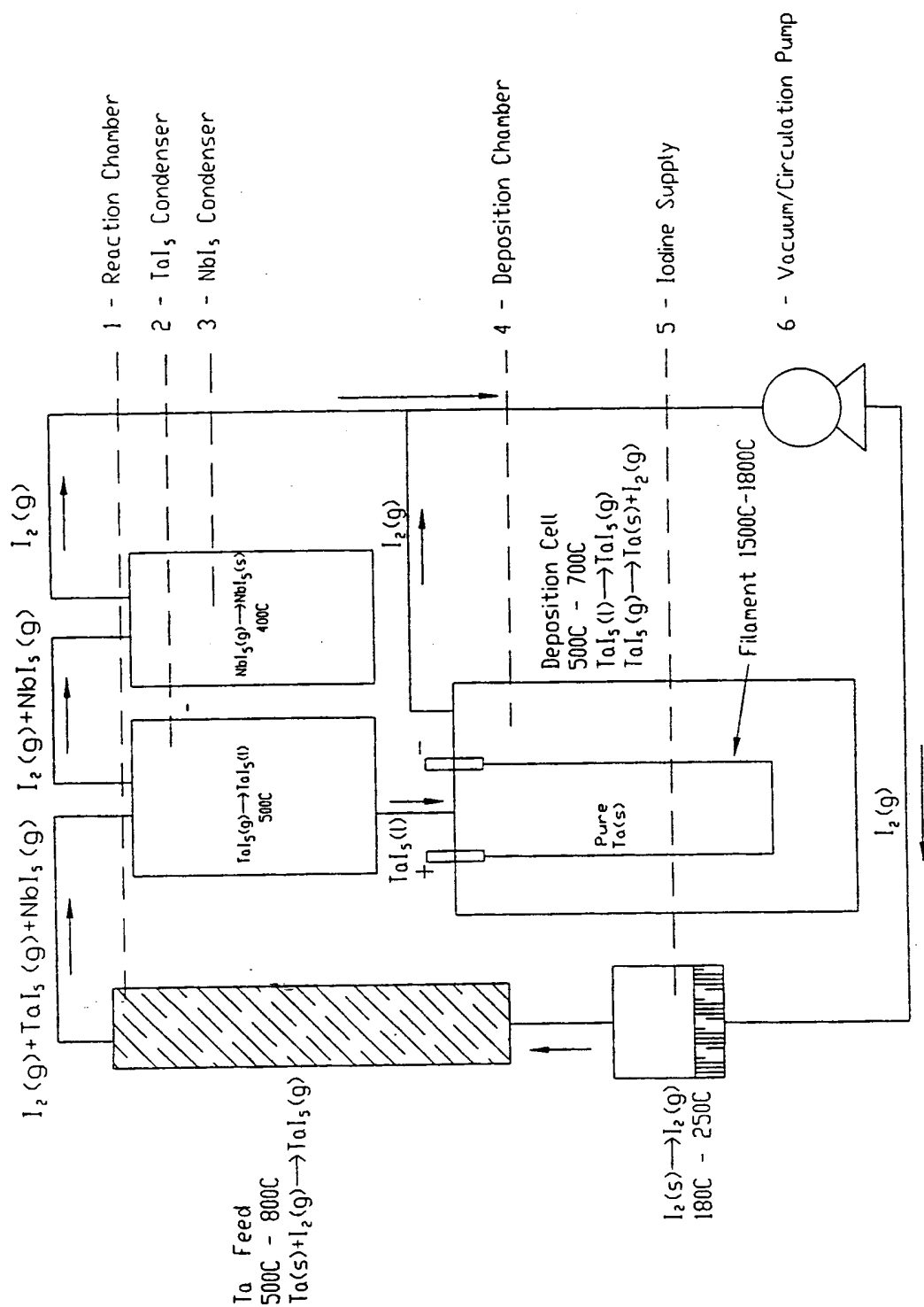


FIG. 3

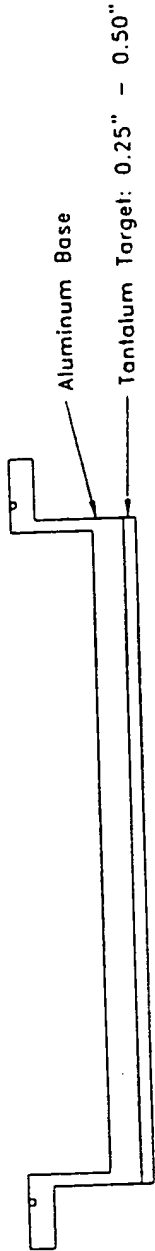


FIG. 4A

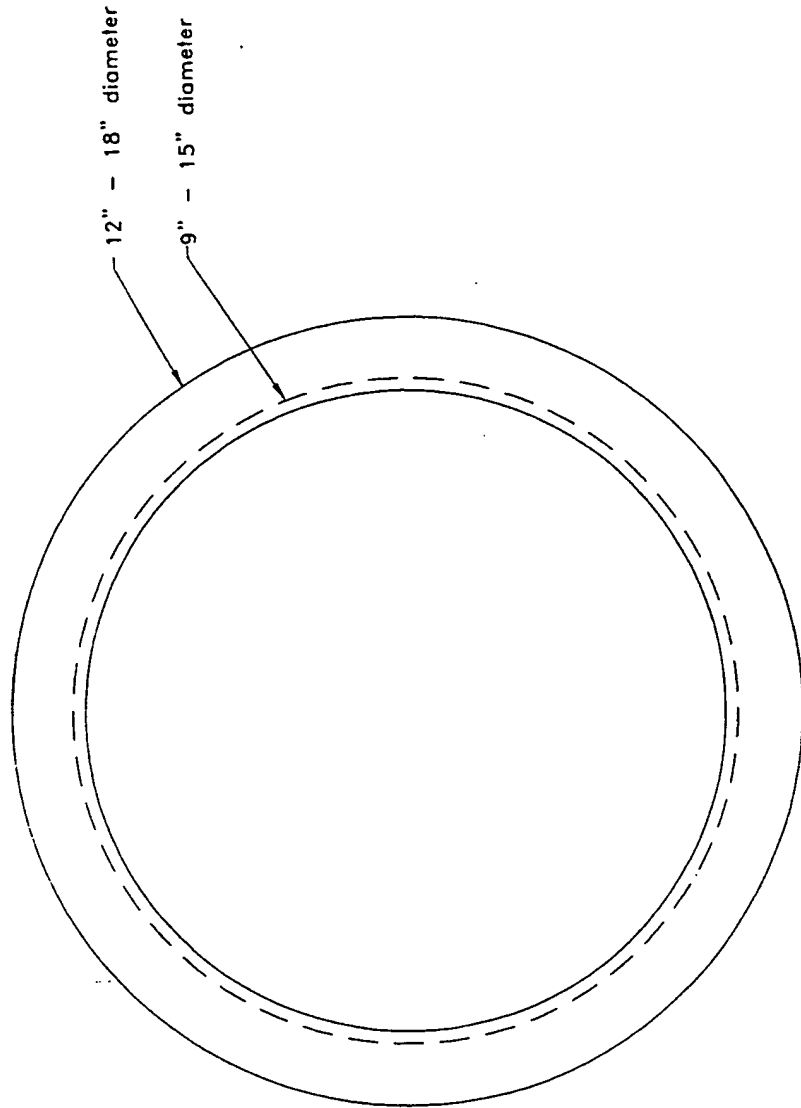


FIG. 4B

5/5

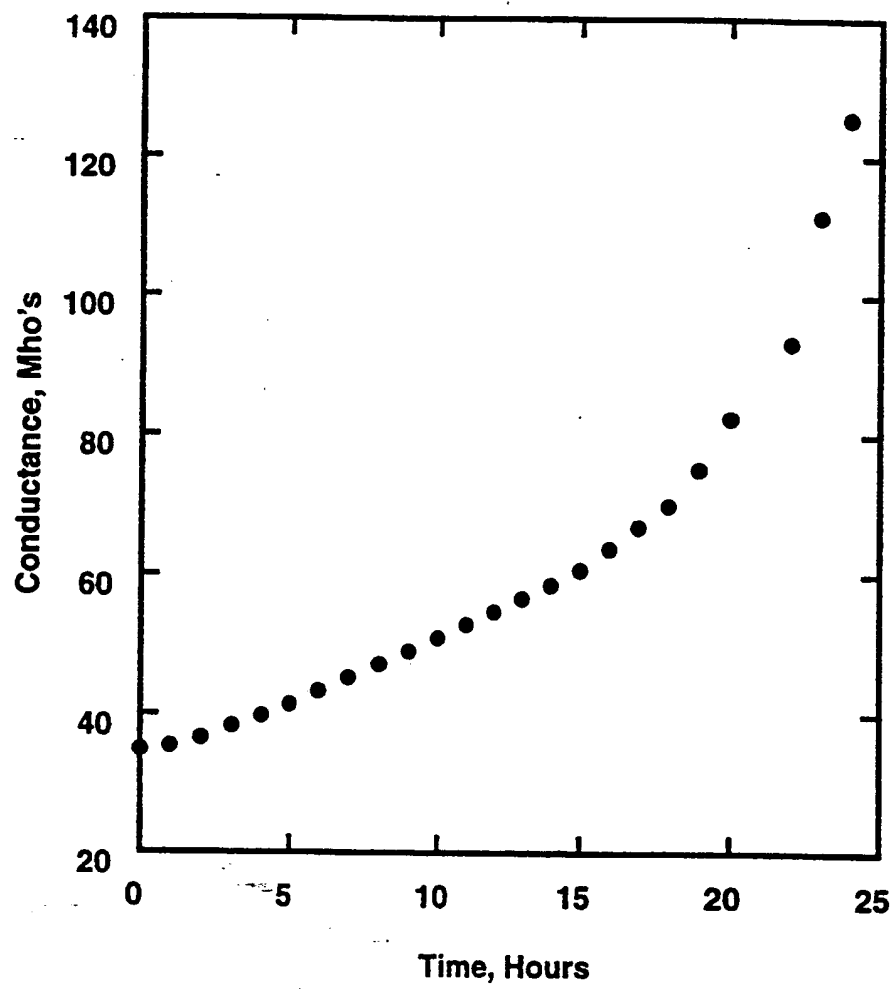


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/11691

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C22B 34/24; C23C 14/34

US CL : 75/10.28, 416, 622; 204/298.13; 420/417; 423/464; 428/472,698

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 75/10.28, 416, 622; 204/298.13; 420/417; 423/464; 428/472,698

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CAPLUS: K2Ta7F5, HF, H2SO4, KCl, iodide, sputtering, tantalum

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	DE 198 41 774 A (SINGH et al) 18 March 1999, see Abstract	1-9 and 15-30
Y	JP03-197640 A (OBATA et al) 29 August 1991, see Abstract	1-30



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

26 AUGUST 1999

Date of mailing of the international search report

19 OCT 1999

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

MELVYN ANDREWS

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/11691

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/11691

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-9 and 15-30, are drawn to a method for producing high purity tantalum comprising purifying potassium heptafluotantalate by a dissolution process, high purity tantalum, a sputtering target and a thin film.

Group II, claim(s) 10-14, are drawn to a method for producing high purity tantalum.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: The invention of Group I claims the special technical feature of purifying potassium heptafluotantalate by a dissolution process which is not found in the invention of Group II.

THIS PAGE BLANK (USPTO)